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| (54) Title: ISOCYANATES AS REACTIVE DILUENTS IN THE PREPARATION OF POLYMERS (57) Abstract This invention describes isocyanate-based vinyl polymer compositions which are useful for the preparation of synthetic polymers. The invention further describes a process wherein ethylenically-unsaturated monomers are substantially polymerized in the presence of isocyanates. | | |

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ISOCYANATES AS REACTIVE DILUENTS IN THE PREPARATION OF POLYMERS

Background Of The Invention

5 The invention relates to isocyanate-based vinyl polymer compositions, specifically to a process wherein ethylenically-unsaturated monomers are polymerized in the presence of isocyanates.

Background Of The Prior Art

10 It is well known that polymers comprising vinyl polymers, polyurethane polymers and/or polyurethane-vinyl polymers can be formed using a combination of free-radical addition and isocyanate chain propagation reactions. The polymers have been shown to be particularly useful as adhesives, binders, coatings and primers. References describing their preparation include:

15 U.S. Patent No. 3,705,164 (Honig et al.) disclose a process wherein vinyl monomers are polymerized, using free-radical initiators, in the presence of anionic polyurethane dispersions.

 U.S. Patent No. 4,318,833 (Guagliardo) disclose a process wherein ethylenically-unsaturated monomers are polymerized, using free-radical initiators, in the presence of
20 water-soluble polyurethanes.

 U.S. Patent No. 4,730,021 (Zom et al.) disclose a process wherein unsaturated urethane dispersions are polymerized, using free-radical initiators, in the presence of ethylenically-unsaturated monomers to form polyurethane-acrylic graft copolymers.

 U.S. Patent No. 4,644,030 (Loewigkeit et al.) disclose a process wherein NCO-
25 terminated polyurethane prepolymers are formed in the presence of ethylenically-unsaturated monomers, dispersed in water, chain extended and polymerized using a free-radical initiator.

 Other related documents include U.S. Patent No. 3,257,476 and 3,291,859 (Tobolsky); U.S. Patent No. 3,624,020 (Klebert et al.); U.S. Patent No. 3,684,758 (Honig
30 et al.); U.S. Patent No. 3,862,074 (Hickey); U.S. Patent No. 3,865,898 (Tobolsky); U.S. Patent No. 4,425,468 (Makhlouf et al.); U.S. Patent No. 4,888,383 (Huybrechts); U.S.

Patent No. 5,095,069 (Ambrose et al.); U.S. Patent No. 5,137,961 (Goos et al.); U.S. Patent No. 5,314,942 (Coogan et al.); and U.S. Patent No. 5,371,133 (Stanley).

A drawback with the processes described in the prior art references relate to the polymerization sequence. The isocyanate reaction is often initiated and completed before the ethylenically-unsaturated monomers are polymerized. In the preparation of aqueous polymer dispersions this sequence can adversely affect the polymer's stability and its physical properties. For example, to complete monomer consumption it is often necessary to extend the free-radical emulsion polymerization process using heat. Under such conditions, sedimentation from ionic destabilization and hydrolysis of the polyester-based polyurethane can degrade the polymer's properties. For these reasons, it would be advantageous to have a process which eliminates the free-radical emulsion polymerization process.

Several advantages associated with using isocyanates as reactive diluents, for the preparation of vinyl polymers, include enhanced processing characteristics and the polymers molecular weight distribution. The single-stage polymerization of ethylenically-unsaturated monomers is enhanced when isocyanates are used as a diluent. For example, said monomers are often stabilized with small quantities of free-radical scavengers having active hydrogen atoms (i.e., hydroquinone). The isocyanates react with said inhibitors, neutralizing their scavenging characteristics, and enhancing the free-radical chain propagation reaction. Additionally, the single-stage solution polymerization can form polyvinyl polymers which are characterized as having a low weight-average (Mw) and number-average (Mn) molecular weight distribution. Such polymers are often useful for the preparation of pressure sensitive adhesives.

Therefore, there remains a need for a process wherein ethylenically-unsaturated monomers are substantially polymerized in the presence of isocyanates.

Summary Of The Invention

To extend the variety and compass of raw materials available for the preparation of synthetic polymers, the present invention discloses isocyanate-based vinyl polymer compositions comprising:

- 1) at least one isocyanate-based compound; and
- 2) at least one vinyl polymer which may contain isocyanate groups;

wherein the vinyl polymer is characterized as having a weight average molecular weight distribution less than about 500,000 grams per mole.

- 5 The compositions can be used for the preparation of synthetic polymers including aqueous polymer dispersions, water dispersible polyfunctional crosslinking agents and solvent-less isocyanate-based polyurethanes (i.e., hot melt moisture cure adhesives).

In another aspect, the present invention discloses isocyanate-based polyvinyl compositions comprising:

- 10 1) at least one isocyanate-based compound; and
- 2) at least one vinyl polymer compound which is the reaction product of;
- a) at least one ethylenically-unsaturated monomer;
 - b) at least one thermally-activated free-radical initiator; and
 - c) optionally, at least one ethylenically-unsaturated oligomer;

- 15 wherein said monomers and oligomers are substantially polymerized in the presence of the isocyanates-based compound.

The invention further discloses a process for the preparation of isocyanate-based vinyl polymer compositions comprising the steps of:

- 20 1) blending a mixture of materials comprising;
- a) at least one isocyanate-based compound;
 - b) at least one ethylenically-unsaturated monomer;
 - c) at least one thermally-activated free-radical initiator; and
 - d) optionally, at least one ethylenically-unsaturated oligomer; then
- 2) heating said mixture to form a vinyl polymer.

25

Detailed Description Of The Invention

The term "vinyl polymer" is defined as a polymer containing two or more free-radically polymerized ethylenically-unsaturated monomers.

- 30 The term "ethylenically-unsaturated monomer" is defined as any compound containing acrylic groups (e.g., α , β -unsaturated carbonyl), vinyl groups, allylic groups and acrylamide groups.

At least one isocyanate compound is used and may include monoisocyanates, polyisocyanates and polymeric polyisocyanates. The isocyanates may be aliphatic, aromatic and mixtures thereof. Examples of commercially available polyisocyanates include Vestanat® IPDI which is isophorone diisocyanate from HULS America Inc.,
5 (Piscataway, NJ); TMXDI® which is tetramethylxylene diisocyanate from Cyanamid (Wayne, NJ); Luxate® HM which is hexamethylene diisocyanate from Olin Corporation (Stamford, CN); diphenylmethane diisocyanate (MDI) from Upjohn Polymer Chemicals (Kalamazoo, MI); Desmodur® W which is dicyclohexylmethane-4,4'-diisocyanate from Mobay Corporation (Pittsburgh, PA); toluene diisocyanate and PAPI® 2094 which is a
10 polymeric MDI from Dow Corning Corporation (Midland, MI). The most preferred isocyanates have low viscosity and low vapor pressures.

Other useful isocyanates include the polyalkoxylated polyisocyanates described in U.S. Patent No. 3,370,077 (Hartzell), U.S. Patent No. 3,631,199 (Smith et al.) and U.S. Patent No. 3,691,223 (Kuder), incorporated herein by reference. These
15 polyisocyanates can be used to enhance the hydrophilic character of the inventive compositions.

Small amounts of isocyanate-functional monomers may be used and include isocyanatoalkyl acrylates and methacrylates such as isocyanatoethyl acrylate, isocyanatopropyl acrylate, isocyanatobutyl acrylate, isocyanatoethyl methacrylate,
20 isocyanatopropyl methacrylate and isocyanatobutyl methacrylate. Other useful isocyanate-functional monomers include those described in U.S. Patent No. 4,632,957 (Welsh, et al.), incorporated herein by reference. Said monomers are polymerized into the vinyl polymer segment to form isocyanate-functional vinyl polymers.

At least one ethylenically-unsaturated monomer is used and may include
25 monounsaturated monomers, polyunsaturated monomers and their mixtures. Examples include methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, n-propylacrylate, isopropyl acrylate, methyl methacrylate, butyl methacrylate, vinyl acetate, vinyl propionate, vinyl ethers, ethylenically-unsaturated fumarates, ethylenically-unsaturated maleates, styrene, acrylonitrile, acrylamides, ethylenically-unsaturated
30 imidazolidinones, ethylenically-unsaturated perfluorinated monomers, butanediol diacrylate, hexanediol diacrylate trimethylolpropane triacrylate. Other useful monomers

include those described in U.S. Patent No. 3,705,164 (Honig, et al.), incorporated herein by reference.

Additionally, monomers having active hydrogen atoms may be used in the present invention. Examples include hydroxyethyl acrylate, vinyl amine and the
5 monomers described in U.S. Patent No. 4,888,383 (Huybrechts), incorporated herein by reference. These monomers can be present in a range from about 0.1% by weight to about 10.0% by weight, and preferably from about 0.3% by weight to about 6.0% by weight, based on total polyvinyl solids. Said monomers react with isocyanates and polymerize into the vinyl polymer segment to form isocyanate-functional vinyl
10 polymers.

Ethylenically-unsaturated oligomers can be used in combination with the ethylenically-unsaturated monomers. Alternatively, it is possible to form an isocyanate-based vinyl polymer composition wherein only said oligomers are polymerized in the presence of the isocyanates. The term "oligomer" is defined as a polymer comprising 2
15 or more covalently linked monomer units. Such oligomers may be hydrophilic or hydrophobic and comprise at least one ethylenically-unsaturated group including acrylic, vinyl, allylic, acrylamide and their mixtures. Examples include the polyester-based acrylates and the polyurethane-based acrylates described in U.S. Patent No. 4,822,829 (Muller et al.), U.S. Patent No. 5,391,602 (Skoultchi) and U.S. Patent No. 4,525,232
20 (Rooney et al.), incorporated herein by reference.

The ethylenically-unsaturated monomers are polymerized using thermally-activated free-radical initiators which are free of active hydrogen atoms. The term "active hydrogen atoms" refers to hydrogens which display activity according to the Zerewitinoff test as described by Kohler in J. Am. Chem. Soc., 49,3181 (1927).
25 Examples include Vazo® 52 (2,2'-azobis[2,4-dimethylvaleronitrile]), and Vazo® 64 (2,2'-azobis [isobutyronitrile]), Vazo® 67 (2,2'-azobis [methylbutyronitrile]) and Vazo® 88 (1,1'-azobis [cyanocyclohexane]) which are commercially available azonitrile compounds from DuPont (Wilmington, DE). The grade number of these products indicate the Celsius temperature at which the azonitriles half-life in solution (toluene) is
30 10 hours. The initiators are readily soluble in the isocyanate/monomer mixture and can be heated to a temperature in a range from about 40°C to about 100°C, and preferably

from about 50°C to about 90°C. Reaction temperatures less than about 100°C are preferred in that temperatures greater than about 100°C can cause isocyanate trimerization and/or isocyanate side reactions. Said initiators can be present in amounts from about 0.01% by weight to about 2.0% by weight, and preferably from about 0.10% by weight to about 0.5% by weight, based on the total weight of the monomer. If desired, said initiators can be photochemically decomposed at a wavelength of about 350nm.

During the thermal decomposition of the azonitrile compounds, inert gases such as nitrogen and argon are often used. These inert gases generate an oxygen-free environment and aid polymerization. For example, the presence of oxygen can inhibit polymerization by scavenging free-radicals.

The isocyanate-based vinyl polymer compositions can be prepared by blending together at least one isocyanate-based compound, at least one ethylenically-unsaturated monomer and at least one thermally-activated free-radical initiator to form a reactive mixture. The mixture is agitated, purged with an inert gas to maintain an oxygen-free environment and heated to form a vinyl polymer. Alternatively, the monomer can be slowly added to the isocyanate-based compound over period of time to control the reaction rate.

The resulting vinyl polymer can have a weight-average molecular weight distribution of from about 2,000 grams per mole to about 1,000,000 grams per mole, and preferably from about 10,000 grams per mole to about 500,000 grams per mole. A weight-average molecular weight distribution less than about 500,000 grams per mole is often preferred when said materials are used for the preparation of adhesives having pressure sensitive characteristics. Lower molecular weight vinyl polymers generally enhance the adhesive tack characteristics.

The vinyl polymers average molecular weight distribution (M_w and M_n) can be modified by adjusting:

- 1) the weight percent of ethylenically-unsaturated monomer in the reaction mixture;
- 2) the weight percent of the thermally-activated free-radical initiator in the reaction mixture; and

- 3) the time and temperature at which the reaction mixture is heated to generate free-radicals.

For example, if a higher molecular weight distribution is desired the reaction mixture comprises:

- 5 1) a higher weight percent of monomer;
- 2) a lower weight percent of initiator; and
- 3) the reaction mixture is heated for an extended period of time at reduced temperatures (i.e., below the half-life decomposition temperature of the initiator).

10 Alternatively, if a lower molecular weight distribution is desired the reaction mixture comprises:

- 1) a lower weight percent of monomer;
- 2) a higher weight percent of initiator; and
- 15 3) the reaction mixture is quickly heated above the half-life decomposition temperature of the initiator.

The inventive compositions can have a weight ratio of isocyanate-based compound to vinyl polymer in a range from about 95:05 to about 05:95, and preferably from about 70:30 to about 30:70, based on the total weight of the composition. If a higher weight ratio of vinyl polymer is desired, solvents which are free of active
20 hydrogen atom may be used to lower the compositions viscosity. The compositions can have viscosities in a range from about 100 m.Pas to about 100,000 m.Pas and preferably from about 100 m.Pas to about 10,000 m.Pas. Lower viscosities are preferred in that such viscosities generally improve processing characteristics and reduce the need for organic solvents.

25 The characteristics of the isocyanate-based vinyl polymer compositions can be modified by the addition of materials, which are preferably free of active hydrogen atoms, including organometallic catalysts, tertiary amine catalysts, surfactants, defoaming agents, coalescing aids, fungicides, bactericides, plasticizers, thickening agents, pigments, dispersing agents for the pigments, colors, perfume-like materials, UV
30 stabilizers, fire retardant agents and organic solvents. Such materials can be introduced at any stage of the production process.

The isocyanate-based vinyl polymer compositions can be used for the preparation of aqueous and non-aqueous polymers including aqueous polymer dispersions, water dispersible polyfunctional crosslinking agents and solvent-less isocyanate-terminated polyurethane prepolymers. The term "polyurethane" is defined as a polymer containing two or more urethane groups and is also intended to cover polyurethane-urea polymers. References illustrating the preparation of such polymers, which may be employed in the practice of the present invention, can be found in U.S. Patent No. 3,479,310 (Dieterich et al.), U.S. Patent No. 4,066,591 and 4,147,679 (Scriven et al.), U.S. Patent No. 4,801,644 (Coogan), U.S. Patent No. 5,334,690 (Schafheutle et al.) and U.S. Patent No. 5,354,807 (Dochniak). Additionally, the compositions can be used for the preparation of polyurethane-based foams.

The inventive compositions and the products formed therefrom can be used as adhesives, binders, coatings or primers and can be applied to substrates including paper, leather, metal, glass, cloth, natural rubber, ceramics and synthetic polymers including acrylonitrile-butadiene-styrene (ABS), polyvinyl chloride and polypropylene. Also, the compositions may be applied on a substrate using application methods known in the art including brushing, roll coating and spraying.

The present invention is illustrated, but not limited by, the following examples wherein the percentages are all by weight.

20

Examples

The following test methods were used:

Viscosity Test

The isocyanate-based vinyl polymer compositions were evaluated using a Brookfield Viscometer Model-RTV from Brookfield Engineering Laboratories, Inc., (Stoughton, MA). Viscosities were measured using a #3 spindle at a setting of 20 revolutions per minute.

Example 1

Example 1 describes the polymerization of n-butyl acrylate in isophorone diisocyanate (IPDI®).

A reaction vessel was charged with 129.3 grams IPDI®, 32.3 grams n-butyl acrylate and 0.24 grams Vazo® 64. The vessel was purged with nitrogen, agitated with mechanical stirring and heated to a temperature in a range from about 65°C to about 100°C for 4 hours. The uniform, clear, colorless isocyanate-based acrylic polymer composition had an isocyanate content of 30.27%, an n-butyl acrylate content of 0.7% +/- 0.1% and a viscosity of 1,580 m.Pas.

Example 2

Example 2 describes the preparation of a perfluorinated butyl acrylate polymer in m-tetramethylxylene diisocyanate (TMXDI®).

A reaction vessel was charged with 224.3 grams TMXDI®, 41.7 grams n-butyl acrylate, 12.4 grams fluoroalkylmethacrylate which is Zonyl® TM from DuPont and 0.42 grams Vazo® 64. The vessel was purged with nitrogen, agitated with mechanical stirring and heated to a temperature in a range from about 65°C to about 100°C for 5 hours. The isocyanate-based acrylic polymer composition had an isocyanate content of 28.21%, an n-butyl acrylate content of 0.3% +/- 0.1%. Residual Zonyl® TM was not detected.

Example 3

Example 3 describes the preparation of an isocyanate-functional acrylate polymer in m-tetramethylxylene diisocyanate (TMXDI®).

A reaction vessel was charged with 435.6 grams TMXDI®, 98.0 grams n-butyl acrylate, 11.0 grams TMI® which is an unsaturated aliphatic isocyanate from Cytec Industries (Wayne, NJ) and 0.182 grams Vazo® 64. The vessel was purged with nitrogen, agitated with mechanical stirring and heated to a temperature in a range from about 65°C to about 100°C for 24 hours. The clear, colorless isocyanate-functional polyacrylic composition had an isocyanate content of 28.28%, an n-butyl acrylate content of 0.5% +/- 0.1% and a TMI® content less than 0.1%. The molecular weight distribution of the polymeric components, relative to polystyrene standards, are diagrammed below:

Gel permeation chromatography (GPC) number average molecular weight of high polymer = 73,600 +/- 2,300 gram/mol.

GPC weight average molecular weight of high polymer = 310,000 +/- 14,000 grams/mol.

5

Example 4

Example 4 describes the preparation of an acrylate polymer in dicyclohexylmethane-4,4'-diisocyanate.

A reaction vessel was charged with 200.0 grams dicyclohexylmethane-4,4'-
10 diisocyanate, 200.0 grams n-methylpyrrolidinone, 75.0 grams methymethacrylate, 25.0 grams n-butyl acrylate and 0.15 grams Vazo® 64. The vessel was purged with nitrogen, agitated with mechanical stirring and heated to a temperature in a range from about 65°C to about 100°C for 6 hours. The isocyanate-based acrylic polymer composition had a methymethacrylate content of 0.2% +/- 0.1%, n-butyl acrylate was undetected and the
15 polymeric weight distribution is described below:

GPC number average molecular weight of high polymer = 21,800 +/- 700 g/mol.

GPC weight average molecular weight of high polymer = 42,200 +/- 1,900 g/mol.

Example 5

20 Example 5 describes the preparation of an aqueous polymer dispersion using the composition described in Example 1.

A reaction vessel equipped with a thermometer, inert gas source and mechanical stirring was charged with 248.49 grams Voranol® 230-112, which is a polyether polyol from Dow Chemical, and 24.31 grams phthalic anhydride. The materials were heated to
25 150°C for 1 hour. After cooling to 50°C the vessel was charged with 122.3 grams of the composition described in Example 1, 120.3 grams isophorone diisocyanate, 668.8 grams Rucoflex® S-1011-55 which is a polyesterether polyol from Ruco Corporation and 30.8 grams triethylamine. The mixture was heated to 80°C for 2 hours and then dispersed in 2,096 grams distilled water using agitation. To the dispersion was charged a mixture
30 containing 8.12 grams monoethanolamine, 13.4 grams ethylene diamine and 70 grams distilled water. The aqueous polymer dispersion properties are described below:

pH = 7.38

Viscosity = 70 m.Pas

Solids = 34.61%

Tg = 35°C +/- 1.0°C

5 Particle size distribution = 79 nm. effective diameter

81 nm. mean diameter

Monomodal distribution

Monomer residuals in emulsion by head space GC = 130 ppm n-butyl acrylate.

10 **Comparative Data**

Example 6

Example 6 describes the preparation of the polymer composition disclosed in Example 5 with the exception the n-butyl acrylate was subjected to free-radical emulsion polymerization.

15 A reaction vessel equipped with a thermometer, inert gas source and mechanical stirring was charged with 248.49 grams Voranol® 230-112, which is a polyether polyol from Dow Chemical, and 24.31 grams phthalic anhydride. The materials were heated to 150°C for 1 hour. After cooling to 50°C, the vessel was charged with 218.3 grams isophorone diisocyanate, 668.8 grams Rucoflex® S-1011-55 which is a polyesterether
20 polyol from Ruco Corporation, 30.8 grams triethylamine and 24.5 grams n-butyl acrylate. The mixture was heated to 80°C for 2 hours and then dispersed in 2,096 grams distilled water using agitation. To the dispersion was charged a mixture containing 8.12 grams monoethanolamine, 13.4 grams ethylene diamine and 70 grams distilled water. The dispersion was then charged with 0.04 grams Vazo® 64 and heated to 65°C an
25 additional 5 hours. The polymer properties are described below:

pH = 7.8

Viscosity = 30 m.Pas

Solids = 35.05%

Tg = -37°C +/- 1.0°C

30 Particle size distribution = 101 nm. effective diameter

107 nm. mean diameter

Monomodal distribution

Monomer residuals in emulsion by head space GC = 860 +/- 170 ppm n-butyl
acrylate

- 5 The residual monomer data (Example 5 & 6) shows the solution polymerization process is more effective at substantially consuming the monomer compared to the emulsion polymerization process, showing the utility of the invention.

Example 7

- 10 Example 7 describes the preparation of a water-based polyurethane-vinyl polymer using the isocyanate-functional vinyl polymer composition described in Example 3.

- A reaction vessel equipped with a thermometer, inert gas source and mechanical stirring was charged with 432 grams Rucoflex® S-1011-55, 21.0 grams dimethylolpropionic acid, 15.0 grams triethylamine, 68.87 grams TMXDI® and 83.75
15 grams of the composition described in Example 3. The materials were heated to about 85°C for 4 hours. The prepolymer was dispersed in 909 grams distilled water and then charged with a mixture containing 10.9 grams ethylene diamine and 25 grams distilled water. The polymer dispersion had a pH of 7.8, a solids content of 38.87% and a
viscosity of 35 m.Pas.

20

Claims

What is claimed is:

1. A isocyanate-based vinyl polymer composition comprising:
 - a) at least one isocyanate-based compound; and
 - b) at least one vinyl polymer wherein said polymer is characterized as having a weight average molecular weight distribution of less than about 500,000 grams per mole.
2. A isocyanate-based vinyl polymer composition comprising:
 - a) at least one isocyanate-based compound; and
 - b) at least one vinyl polymer which is the reaction product of;
 - 1) at least one ethylenically unsaturated monomer;
 - 2) at least one thermally-activated free-radical initiator; and
 - 3) optionally, at least one ethylenically-unsaturated oligomer;wherein the ethylenically-unsaturated groups are polymerized in the presence of said compound to form a vinyl polymer.
3. A process for the preparation of vinyl polymer compositions comprising the steps of:
 - 1) blending a mixture of materials comprising;
 - a) at least one isocyanate-based compound;
 - b) at least one ethylenically-unsaturated monomer; and
 - c) at least one thermally-activated free radical initiator; then
 - 2) heating said mixture to polymerize said monomer in the presence of said compound to form a vinyl polymer composition.
4. The composition described in Claim 1, 2 or 3, wherein said compound is selected from the group consisting of aliphatic isocyanates, aromatic isocyanates and mixtures thereof.
5. The composition as described in Claim 4, wherein said compound is selected from the group consisting of monoisocyanates, polyisocyanates, polymeric polyisocyanates and mixtures thereof.
6. The composition as described in Claim 1, 2 or 3, wherein said compound is present in a range from 95 parts by weight to 5 parts by weight, and said vinyl polymer is present in a range from 5 parts by weight to 95 parts by weight.

7. The composition as described in Claim 1,2 or 3, wherein said monomer is selected from the group consisting of monounsaturated monomer, polyunsaturated monomers and mixtures thereof.
8. The composition as described in Claim 7, wherein said monomer is selected from the group consisting of acrylic, vinyl, allylic, acrylamide and mixtures thereof.
9. The composition as described in Claim 1,2 or 3 wherein said initiator is an azonitrile.
10. The composition as described in Claim 9, wherein said initiator is selected from the group consisting of 2,2'-azobis (2,4-dimethylvaleronitrile), 2,2'-azobis (isobutylironitrile), 2,2'-azobis (methylbutylironitrile), 1,1'-azobis (cyanocyclohexane) and mixtures thereof.

INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/US 97/19534

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F2/06 C08F246/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No |
|----------|--|----------------------|
| X | FR 2 234 340 A (IMPERIAL CHEM. IND. LTD.) 17 January 1975 see claims 1,2 | 1-10 |
| A | FR 1 138 102 A (BAYER) 11 June 1957 | |
| A | DE 42 37 030 A (BASF) 5 May 1994 | |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex

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